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Second positive bands of N_2 in the afterglow of N_2 and O_2 mixture

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(Plate—6)

The second positive bands of N_2 were observed in the afterglow of N_2 and O_2 mixture and were studied spectroscopically, photometrically and microphotometrically. Effect of temperature on the intensity of bands at 3371Å and 3577Å of N_2 $2PG$ system is small. Quenching cross-sections for the above by N_2 and O_2 are of the order of 10^{-14} cm^2 and 10^{-15} cm^2, respectively. Excitation mechanism of these bands in the laboratory has been proposed as follows :

$$N+O+N_2 \rightarrow NO+N_2(A^3\Sigma_u^+)$$

$$O+O+N_2(A^3\Sigma_u^+) \rightarrow O_2+N+(C^3\Pi_u)$$

$$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)+h\nu$$

Introduction

Mecke & Lindau (1924) and Coster *et al* (1933) observed the second positive bands of N_2 in the discharge of N_2 and air and also in arcs at low pressures. These bands were also excited by bombarding N_2 molecules by ions (Philpot *et al* 1961, Ghosh *et al* 1965). In the pink afterglow excited in highly pure N_2, the presence of the bands was detected and their excitation was discussed by Piag & Clark (1963). The afterglow excited in N_2 of ordinary purity contains mainly first positive bands and very weak second positive bands (Young & Black 1966). Barth & Kaplan (1957) observed the N_2 second positive bands in the afterglow of N_2 containing 2 percent of oxygen.

To understand the excitation mechanism of these bands in the afterglow and their characteristics, the present investigation was undertaken.

Experimental Arrangement and Observations

The experimental system described elsewhere (Ghosh *et al* 1969a) has been used omitting the sodium vapouring chamber (figure 1). N_2 and O_2 gases were used directly from cylinder without purification. These gases were 99·5% pure. Oxygen gas was introduced through the needle valve N' and was dissociated by discharge from a microtherm before it entered the reaction chamber. The

N_2 gas was introduced through the other needle valve N'. After adjusting the flow rates of N_2 and O_2 gases, the maximum intensity in the afterglow was obtained. A strong white-greenish afterglow filled the reaction chamber. When the flow of O_2 was stopped, afterglow did not appear in the reaction chamber even with large flow rate of N_2.*

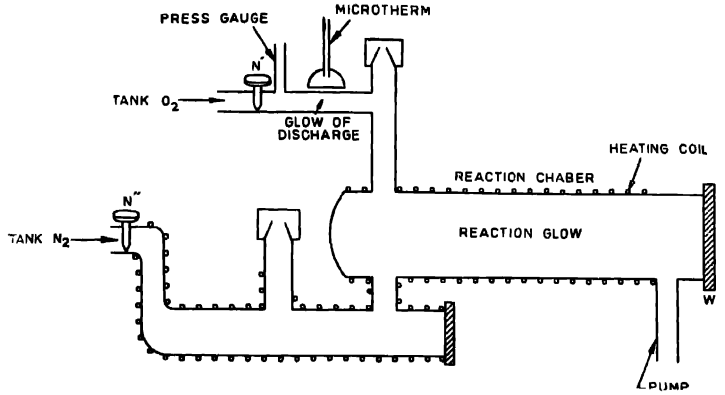


FIGURE 1. Experimental arrangement for the study of the afterglow.

Spectroscopic and photometric observations, and microphotometric analysis of the afterglow are described below.

1. *Spectroscopic* : The spectrum of the afterglow was taken with a Hilger medium quartz spectrograph through the quartz window W (plate 6). An exposure of 12 hours was given on Kodak F(103)a plate. It was observed that N_2 second positive bands in the range 3000–4500 Å were present.** The bands and their visual intensities are given in table 1.

2 *Photometric observations* : Second positive bands of N_2 at 3371Å and 3577Å were selected by a monochromator described elsewhere (Ghosh *et al* 1969a). Three photometric observations were carried out, namely, variation of intensities of 3371Å and 3577Å with (1) N_2 pressure at a fixed flow rate of O_2. (2) O_2 pressure at a fixed flow rate of N_2, and (3) temperature. These observations are described below :

* Afterglow produced by dissociating N_2 molecules was investigated and was studied in great detail by Young & Black (1966). In the present experimental setup, however, the N_2 gas was not directly under microtherm discharge.

** Actually N_2 second positive bands were observed in the range 3000–4500Å. The bands above this wavelength region were too weak to be observed.

TABLE 1. N_2 Second positive bands observed in the afterglow of O_2 and N_2 mixture; ($B^3\Pi_g - C^3\Pi_u$)

Band head (Å)	Intensity (visual)	Transition
3104	VVF	4,3
3116	VF	3,2
3336	F	2,1
3159	S	1,0
3268	VF	4,4
3285	VF	3,3
3309	VVF	2,2
3339	VVF	1,1
3371	VVS	0,0
3501	S	2,3
3537	VS	1,2
3577	VVS	0,1
3642	VVF	4,6
3672	S	3,5
3711	VS	2,4
3755	VVS	1,3
3805	VVS	0,2
3860	VVF	4,7
3895	VF	3,6
3943	S	2,5
3998	VS	1,4
4059	S	0,3
4095	F	4,8
4142	F	3,7
4200	F	2,6
4270	VVF	1,5
4344	VVF	0,4
4355	VVF	4,9

(*i*) *Variation of intensities of* 3371Å *and* 3577Å *with* N_2 *pressure*

The intensity of band at 3371Å was measured at different pressures in the range 100-650 μ (figure 2) and for the band at 3577Å, in the range 90–700 μ (figure 3). The flow rate of O_2 was kept constant. It was observed that the intensities of these bands at first rise with N_2 pressure and then, after attaining a maximum in the pressure range 300-400 μ begin to fall For both these bands, the rise of intensity before reaching maximum values can be represented approximately by $I = K_1 p$, where I is the intensity at a pressure p, K_1 is a constant The fall of intensities after reaching maximum values is given by $Ip = K_2$, where I, p and K_2 have their usual meanings.

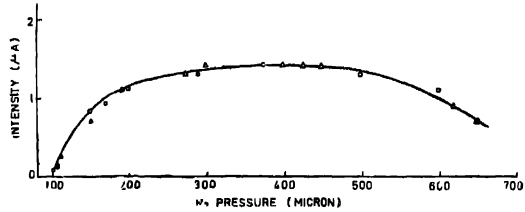


FIGURE 2 The intensity of the band at 3371Å is plotted against N_2 pressure at a fixed flow rate of O_2. Note the flat maximum in the pressure range 340–460μ

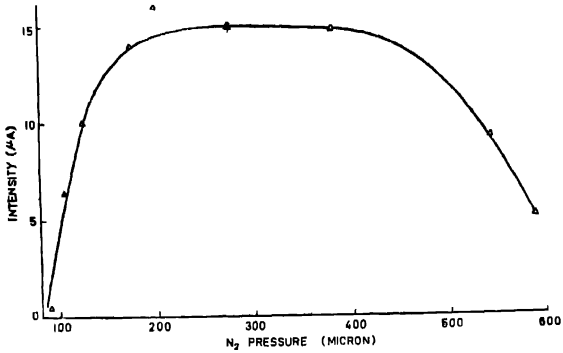


FIGURE 3 The intensity of the band at 3577Å is plotted against N_2 pressure at a fixed flow rate of O_2. Note the flat maximum in the pressure range 220–400μ.

(*ii*) *Variation of intensities of* 3371Å *and* 3577Å *with* O_2 *pressure*

Keeping the flow rate of N_2 fixed, the variation of intensities of these bands at different pressures in the range 85–200 μ (figure 4) and 100–450 μ (figure 5), respectively, were measured. It was observed that the quenching of these radiations by O_2 was considerable and is strong even at small concentration. The fall of intensities of the bands at 3371Å and 3577Å with the increase of O_2 pressure can be represented approximately by $Ip^3 = K_3$ and $Ip^4 = K_4$, respectively, and I, p, K_3 and K_4 have their usual significances.

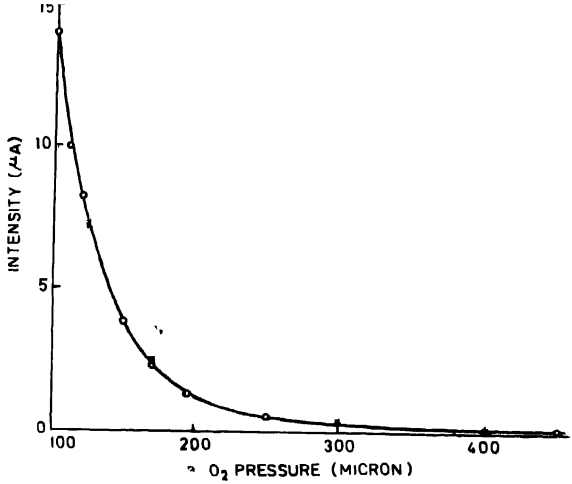


FIGURE 4. The intensity of the band at 3371Å is plotted against O_2 pressure at a fixed flow rate of N_2. Note that O_2 quenches the band considerably.

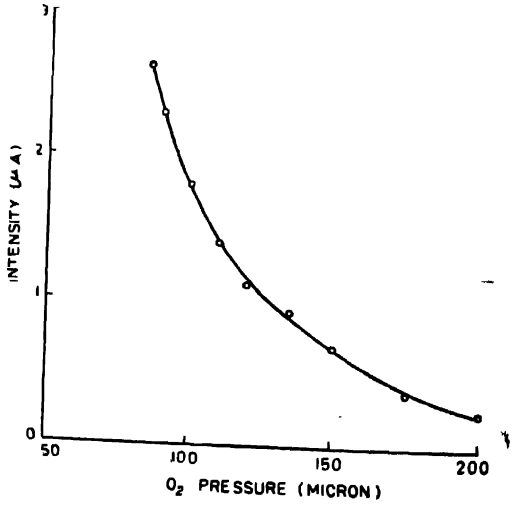


FIGURE 5. The intensity of the band at 3577Å is plotted against O_2 pressure at a fixed flow rate of N_2. Note that O_2 quenches the band considerably.

(iii) Variation of intensities of 3371Å *and* 3577Å *with temperature*

The intensities of these bands were measured at different temperatures in the range 25–325°C by heating the chamber electrically (figure 6). The temperature of the chamber was measured by a pyrometer (Ghosh *et al* 1969b).

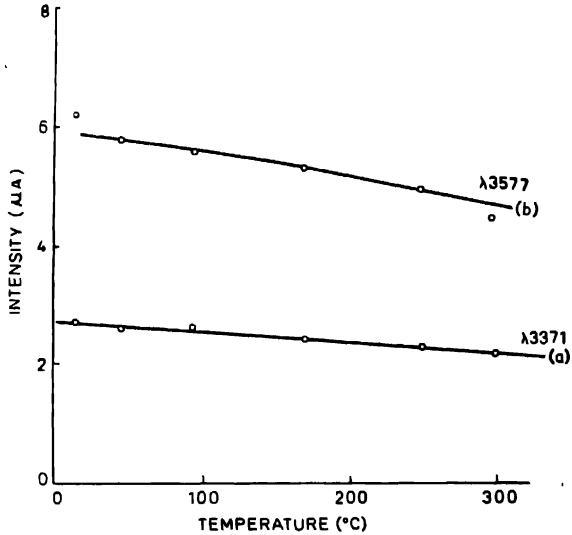


FIGURE 6 The intensities of bands at 3371Å and 3577Å are plotted against temperature. The intensity varies slightly with temperature.

It was observed that the effect of temperature on the bands at 3371Å and 3577Å is very small. The fall of intensities of these bands is small and can be represented by

$$I = \alpha T + I_0$$

where I_0 and I are the intensities at room temperature and at T°C. α is a constant and is negative. The values of α obtained from figure 6 are approximately $1{\cdot}84\times10^{-3}$ μA/°C and $2{\cdot}92\times10^{-3}\mu A$/°C for 3371Å and 3577Å respectively.

(iv) Microphotometric analysis

The N_2 second positive bands were scanned from 3000Å to 5000Å by a microphotometer described elsewhere (Ghosh *et al* 1969b) (figure 7). By measuring areas covered by the bands, the relative intensities of N_2 second positive bands are obtained and are given in table 2.

TABLE 2. Relative intensities of second positive system of N_2

Band head (Å)	Transition	Relative Intensity
3576.9	0,1	1.00
3371.3	0,0	0.96
3536.7	1,2	0.75
3159.3	1,0	0.65
3755 4	1,3	0.56
3804.9	0,2	0.55
3136.0	2,1	0.48
4059 4	0,3	0 47
3998.4	1,4	0.47
3943.0	2,5	0.45
3894 6	3,6	0.43
3710.5	2,4	0.41
3285.3	3,3	0 38
3500.5	2,3	0.31
3268.1	4,4	0.30
3857.9	4,7	0.22
3671.9	3,5	0.22
3641.7	4,6	0.18

CALCULATION OF QUENCHING COEFFICIENTS

The quenching coefficients have been calculated from figures 2 & 3 by utilizing the curves from maximum intensity till it falls to half of its value The coefficients have been obtained from the formula ·

$$K = \frac{A}{n' - 2n_M}$$

where A = transition probability,

n' = concentration of the quenching species at half intensity, and

n_M = concentration for maximum intensity

The quenching coefficients and quenching cross-sections for the bands at 3371Å and 3577Å by N_2 and O_2 are given in table 3

TABLE 3. Quenching coefficients and quenching cross-sections for bands at 3371Å and 3577Å

Band head (Å)	Quenching species	Quenching coefi (cm³/molecule-sec)	Quenching cross-section (cm²)
3371	O_2	$1\ 1\times10^{-9}$	5.0×10^{-14}
3371	N_2	$1\ 9\times10^{-9}$	$2\ 2\times10^{-15}$
3577	O_2	1.3×10^{-9}	$6\ 5\times10^{-14}$
3577	N_2	1.0×10^{-9}	5.2×10^{-15}

Discussion

To excite the N_2 second positive bands, high energy (nearly 11 eV) is required The photometric study carried out in the present investigation suggests the following mechanism for its excitation

N and O atoms may recombine in the presence of N_2 as a third body forming NO molecules. An amount of 6·5 eV energy (dissociation energy of NO, Wilkinson 1963) will be released during the reaction, which will raise N_2 to $A^3\Sigma_u^+$ state requiring nearly 6·2 eV·

$$N+O+N_2 \xrightarrow{K_1} NO+N_2\ (A^3\Sigma_u^+) \qquad \ldots (1)$$

$A^3\Sigma_u^+$ is a metastable state having a lifetime greater than 9 seconds (Nicholls 1964) These excited N_2 molecules may be lost as follows :

$$N_2(A^3\Sigma_u^+)+N_2 \xrightarrow{K_2} N_2'+N_2' \qquad \ldots (2)$$

$$N_2(A^3\Sigma_u^+)+O_2 \xrightarrow{K_3} N_2'+O_2' \qquad \ldots (3)$$

$$N_2(A^3\Sigma_u^+) \xrightarrow{A} N_2+h\nu \qquad \ldots (4)$$

where N_2' and O_2' are energetic species and A is the transition probability corresponding to N_2 Vegard-Kaplan bands At equilibrium, one obtains

$$[N_2(A^3\Sigma_u^+)] = \frac{K_1[O][N][N_2]}{K_2[N_2]+K_3[O_2]+A} \qquad \ldots (5)$$

Since [N] and [O] are proportional to $[N_2]$ and $[O_2]$ respectively,

$$[N_2(A^3\Sigma_u^+)] = K\,\frac{[N_2]^2[O_2]}{A+K_2[N_2]+K_3[O_2]} \qquad \ldots (6)$$

where $K = K_1\ K_a$ and K_b.

K_a and K_b are the rate coefficients for dissociation of N_2 and O_2 molecules. From equation (6), since A is small, at a small flow rate of N_2, $[N_2(A^3\Sigma_u^+)]$ will be independent of O_2 pressure. On the other hand, if the fixed flow rate of O_2 is small, $[N_2(A^3\Sigma_u^+)]$ will vary linearly with N_2 pressure.

N atoms can also be removed from the system by the following reaction which is very fast (Schiff 1964)

$$N+NO \rightarrow N_2+O \qquad \ldots (7)$$

Since in both reactions (1) and (7) N atoms are removed and the flow rate of N_2 used in the experiment is low, [N] will be small, so much so that it will

limit the production of $N_2(A^3\Sigma_u^+)$. In other words, the increase of O_2 pressure will not affect the $[N_2(A^3\Sigma_u^+)]$.

The $N_2(A^3\Sigma_u^+)$ may be excited to $N_2(C^3\Pi_u)$ state as follows :

$$O+O+N_2(A^3\Sigma_u^+) \rightarrow O_2+N_2(C^3\Pi_u) \quad \ldots (8)$$

The excited N_2 molecules may be lost as follows :

$$N_2(C^3\Pi_u) \xrightarrow{A} +N_2(B^3\Pi_g)+h\nu \quad \ldots (9)$$

where A is the probability for $B^3\Pi_g - C^3\Pi_u$ transition.

We have already shown in figure 4 and 5 that the second positive bands of N_2 are quenched when O_2 pressure is increased. This can be explained from the fact that in reactions (1) and (7), O atoms remain conserved. There is enough O atoms in the system for the reaction (8) to take place. Increase of O_2 pressure leads to further production of O (O atoms are produced by dissociation of O_2) which quenches of the radiation.

$N_2(C^3\Pi_u)$ molecules may be quenched as follows :

$$N_2(C^3\Pi_u)+N_2 \xrightarrow{K_{10}} N_2'+N_2' \quad \ldots (10)$$

$$N_2(C^3\Pi_u)+O_2 \xrightarrow{K_{11}} O_2'+N_2 \quad \ldots (11)$$

$$N_2(C^3\Pi_u)+O \xrightarrow{K_{12}} N_2+O' \quad \ldots (12)$$

where N_2', O_2' and O' have got their usual meanings.

From equations (8) to (12), the intensity at any pressure is given by,

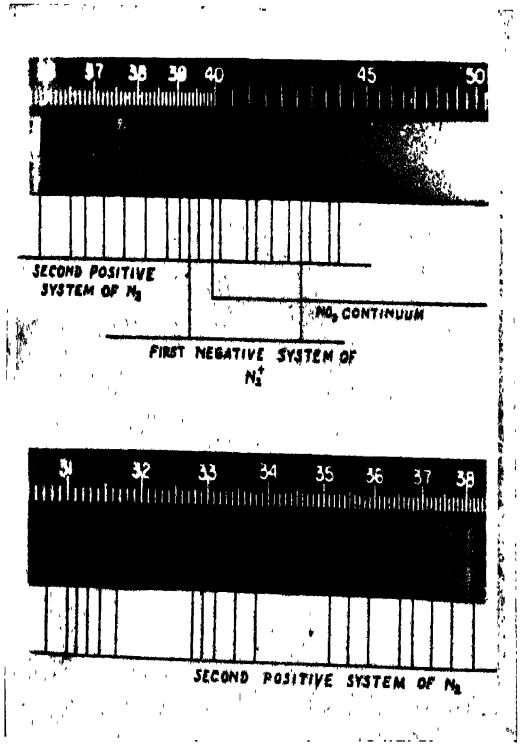
$$I = \frac{K_8[O]^2[N_2(A^3\Sigma_u)]}{1+\frac{K_{10}}{A}[N_2]+\frac{K_{11}}{A}[O_2]+\frac{K_{12}}{A}[O]} \quad \ldots (13)$$

As the N_2 second positive bands have allowed transitions (transition probability $\sim 10^7$ sec^{-1}) and the quenching terms in the denominator of (13) are < 1 at a small flow rate of N_2 ($[O_2]$ and $[O]$ are small). The intensity I will at first vary linearly with increase of N_2 pressure ($N_2(A^3\Sigma_u^+)$ is shown above to vary linearly with N_2). When $[N_2]$ is large so much so that $\frac{K_{10}}{A}[N_2] > 1$, I will be independent of $[N_2]$ (See the flat part of the curves of figures 2 and 3). However, equation (13) fails to explain decrease of intensity I in figures 2 and 3.

The quenching coefficients K_{10} and K_{11} of bands at 3371Å and 3577Å are given in table 2. Their values lie in the range 10^{-8}–10^{-9} cm^3 /molecule-sec. This agrees with the quenching coefficient (10^{-8} cm^3 sec^{-1}) for CN bands by

Indian J. Phys. Volume **44**, *No. 3, 1970*

PLATE 6



Spectrum of the afterglow of N_2 and O_2 mixture showing N_2 second positive bands in the range 3000Å-5000Å

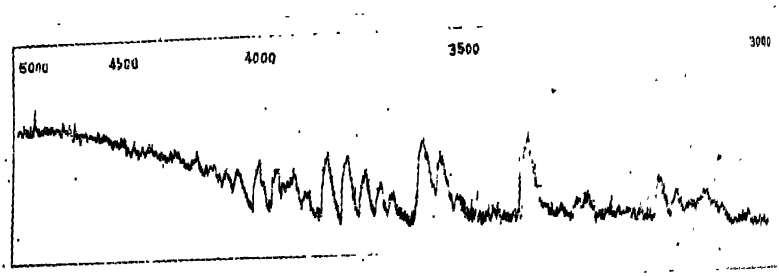


Figure 7. The microphotometer trace of the spectrum of the afterglow in N_2 and O_2 mixture in the range 3000Å-5000Å

CH_2Cl_2 molecules obtained by Ghosh *et al* (1963), and that of $N_2(A^3\Sigma_u^+)$ by N atoms (10^{-10} cm^3 sec^{-1}) obtained by Krassovsky and Shefov (1962) (the quenching by molecules are expected to be larger than by atoms).

Figure 4 shows a slight decrease in the intensities of 3371Å and 3577Å bands with the increase of temperature. The decrease may be due to the increase of quenching coefficient with temperature. It was also observed by Ghosh *et al* (1963).

From the investigations carried out in this paper the following conclusions may be drawn.

(1) For the excitation of second positive bands in the N_2 afterglow, the presence of O is essential.

(2) The quenching of second positive system by O_2 is much larger compared to that by N_2.

(3) Like N_2 first positive bands, these bands have a small negative temperature coefficient.

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